# A Model for the UV-irradiation of Eumelanin supports Dual Functionality at Solar UV-Intensity

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Although it is well established that eumelanin can be both UV-photosensitiser and radical scavenger it's biological role remains unclear. ESR detection of superoxide in UV-irradiated DL-dopa melanin was reported in 1978 [1]; however, Persad *et al*. could only detect superoxide radicals in melanins isolated from red but not black hair [2]. Studies to assess photodamage by UV-irradiated melanins conflict [3,4]; and measurement of hydrogen peroxide production suggests dopa melanin is a photosensitiser over a wide concentration range [5], contrasting an earlier study demonstrating scavenging properties of the pigment [6].

Radical detection is complicated by insolubility of the pigment after isolation by conventional methods; and instability of the radical-adduct of DMPO at pH 7. DMPO-$O_2H^{\cdot}$, however, is readily detected at pH 4.5: since some evidence suggests that the melanosome is acidic; radical production at pH 4.5 and pH 7 is similar (UV absorption to produce semiquinone radicals that disproportionate or donate an electron to oxygen), radical production by UV-irradiated, soluble, DL- and L-dopa melanins at different concentrations was investigated using DMPO at pH 4.5. At a fluence comparable to solar UV, production of the hydroperoxyl radical-adduct increases initially with concentration until about 0.3 mg/ml before subsequently decreasing with further concentration increase. The concentrations of DMPO-$O_2H^{\cdot}$ (observed to be steady state) are consistent with those predicted by a simple model based upon UV absorption and radical scavenging; and which assumes semiquinone-radical reduction of oxygen is fast compared to disproportionation. The data supports a previously hypothesised biological dual role for melanins at solar UV fluence.

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